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SPECTRAL THEORY OF PHYSICAL AND CHEMICAL BINDING: ASPECTS OF COMPUTATIONAL IMPLEMENTATION[a]

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ABSTRACT

Progress is reported in the development and implementation of a spectral method for constructing the adiabatic electronic potential energy surfaces of large heterogeneous aggregates of physically or chemically interacting atoms. The work carries forward a program of study initiated some years ago by W. Moffitt to describe aggregate electronic structure solely in terms of the properties of atoms and their pairwise interactions. Necessary and sufficient conditions are described for construction of the transformation from diatomic to spectral-product states, and of the corresponding pair-interaction Hamiltonian matrices required in the development, employing representatives of the diatomic spectral response operator obtained from Fourier expansion of the Coulombic interactions. These conditions help to advance the development of the spectral method as a practical computational tool for electronic structure determinations employing conventional irreducible-symmetry methodology. The approach is illustrated with computational studies of avoided crossings in the potential energy surfaces of small van der Waals bonded $NaAr_N$ aggregates, which serve as useful prototypes for understanding selected attributes of cryogenic high energy density matter (HEDM). An outline is provided of work in progress on general implementation of the spectral method and of its application to cryogenic fuels and oxidizers seeded with trace metals which may exhibit improved combustion performance.

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I. Introduction

Development of high-specific-impulse cryogenic fuel-oxidizer combinations employing metal or other seedant materials is an important and continuing focus of the USAF high energy density matter (HEDM) program [1]. Accurate adiabatic electronic potential energy surfaces can provide information useful for understanding the structure, stability, and other attributes of such heterogeneous systems. Accordingly, methods for constructing *ab initio* potential energy surfaces which are applicable to large aggregates of physically or chemically interacting atoms are presently under development employing a previously described spectral method devised specifically for this purpose [2].

In the present report, development and implementations are described of the spectral method, and illustrative computational applications are presented in cases of avoided crossings in the potential energy surfaces of physically bonded (van der Waals) inert-gas Ar_N aggregates seeded with metal Na radicals [3]. The general spectral method, which carries forward a program of study initiated some years ago by W. Moffitt [4] and developed and modified by others [5-10], employs a direct product of complete sets of atomic spectral eigenfunctions to represent the total adiabatic electronic wave functions. The representation of the electronic degrees of freedom obtained in this way is not symmetrical [11], and individual terms in the many-electron product basis are not explicitly antisymmetric in the electronic spin and spatial coordinates [12,13]. The Hamiltonian matrix obtained in the spectral-product representation is rigorously pairwise additive in the individual atomic-interaction matrices, which can be obtained by performing calculations on a limited number of appropriate diatomic molecules employing conventional computational methodology. This attribute of the spectral method can provide significant computational advantages for large aggregates of interacting atoms, although issues associated with convergence to antisymmetric states must addressed in the course of its general implementation.

Methods are described here for constructing the required spectral-product basis and the associated pairwise-additive atomic-interaction Hamiltonian matrices from diatomic molecular eigenstates and previously defined spectral response matrices [2] calculated employing conventional computational techniques at finite and asymptotic ($R \rightarrow \infty$) internuclear separations. These methods provide an explicit prescription for constructing the unitary transformation from diatomic to spectral-product representations, advancing the development of the spectral method as a computational tool for electronic structure determinations. The attributes of the approach are illustrated quantitatively with calculations of avoided crossings in the potential energy surfaces of $NaAr_N$ clusters employing diatomic states constructed for this purpose in a finite representational basis.

Aspects of the formal theoretical development are briefly reviewed in Section II, the necessary and sufficient conditions for explicit construction of the unitary transformation from diatomic to spectral-product basis representations are reported in Section III, and illustrative applications to avoided crossing situations in ($NaAr_N$) van der Waals aggregates are reported in Section IV. Concluding remarks and an outline of work in progress on general implementation of the spectral method and its application to physically and chemically bonded HEDM systems is given in Section V.

II. Review of the Theoretical Development

The theoretical development employs a direct product basis of the spectral eigenstates of the individual atoms to represent the correctly antisymmetric aggregate states, which basis provides certain advantages in the study of interacting atoms [2]. Specifically, when the product basis

$$\mathbf{\Phi}(\mathbf{1};\mathbf{2};\ldots;\boldsymbol{n}) = \left\{\mathbf{\Phi}^{(1)}(\mathbf{1}) \otimes \mathbf{\Phi}^{(2)}(\mathbf{2}) \otimes \cdots \mathbf{\Phi}^{(N)}(\boldsymbol{n})\right\}_O \tag{1}$$

is employed in a conventional linear variational solution of the many-electron Schrödinger equation for an aggregate of atoms 1 to N, the Hamiltonian matrix takes the form

$$\mathbf{H}(\boldsymbol{R}) = \sum_{\alpha=1}^{N} \left\{ \mathbf{H}^{(\alpha)} + \sum_{\beta=1}^{N} (\beta > \alpha)\ \mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \right\}, \tag{2}$$

where

$$\mathbf{H}^{(\alpha)} = \left\{\mathbf{E}^{(\alpha)} \otimes \mathbf{I}^{(\beta)} \otimes \mathbf{I}^{(\gamma)} \otimes \cdots \mathbf{I}^{(N)}\right\}_O, \tag{3a}$$

$$\mathbf{E}^{(\alpha)} = \langle \mathbf{\Phi}^{(\alpha)}(\boldsymbol{i}) | \hat{H}^{(\alpha)}(\boldsymbol{i}) | \mathbf{\Phi}^{(\alpha)}(\boldsymbol{i}) \rangle, \tag{3b}$$

are the atomic terms, and

$$\mathbf{V}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \left\{\mathbf{v}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) \otimes \mathbf{I}^{(\gamma)} \otimes \mathbf{I}^{(\delta)} \otimes \cdots \mathbf{I}^{(N)}\right\}_O, \tag{4a}$$

$$\mathbf{v}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \langle \mathbf{\Phi}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}) | \hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}) | \mathbf{\Phi}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}) \rangle, \tag{4b}$$

are the pair-interaction terms. In Eqs. (1) to (4), $\hat{H}^{(\alpha)}(\boldsymbol{i})$ is the atomic Hamiltonian operator for the atom α containing the set of electrons $\boldsymbol{i}$, $\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j})$ is the Coulombic interaction operator for atoms α and β, $\mathbf{\Phi}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j})$ is the spectral-product basis for the indicated pair, a semi-colon is employed to separate sets of distinguishable electrons $(\boldsymbol{i};\boldsymbol{j})$, the bracket symbol $\{\cdots\}_O$ implies choice of a particular ordering rule for the indices of the direct product ($\otimes$) functions, and the vector $\boldsymbol{R}$ specifies the atomic positions.

Because the representation of Eqs. (1) to (4) is not symmetrical [11], the individual products in the basis of Eq. (1) are not totally antisymmetric [12,13], and the Hamiltonian matrix of Eq.(2) can contain terms which do not correspond to physically meaningful (totally antisymmetric) aggregate eigenstates. These can be removed by performing a series of pairwise unitary transformations on the spectral-product basis and the associated Hamiltonian matrix which leave the physical eigenvalues and vectors invariant, but which allow unphysical components to be discarded. The result of these transformations is to replace the matrix elements of Eq. (4b) with the generally different quantities $\mathbf{v}_{sp}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})$ given by the expression

$$\mathbf{v}_{sp}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{T}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{v}_{d}^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{T}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}), \tag{5a}$$

where

$$\mathbf{v}_d^{(\alpha,\beta)}(R_{\alpha\beta}) = \langle \Psi^{(\alpha,\beta)}(i,j)|\hat{V}^{(\alpha,\beta)}(i;j)|\Psi^{(\alpha,\beta)}(i,j)\rangle \tag{5b}$$

is the pair-interaction matrix in the physically meaningful portion of the diatomic eigenstate basis $\Psi^{(\alpha,\beta)}(i,j)$. Here, $\mathbf{T}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta})\cdot\mathbf{D}^{(\alpha,\beta)}(\omega_{\alpha\beta})$, where $\mathbf{D}^{(\alpha,\beta)}(\omega_{\alpha\beta})$ is a product of Wigner rotation matrices for the atoms α and β, the angles $\omega_{\alpha\beta}$ specify the direction of atom β from atom α, and $\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta})$ is the unitary transformation from the physically meaningful (antisymmetric) diatomic states to the spectral-product basis in a pair of rotated atomic coordinate systems having co-linear quantization axes [7].

III. Construction of the Pairwise Rotations

Necessary and sufficient conditions for *ab initio* construction of the pair transformations $\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta})$ are obtained from the expression

$$\mathbf{v}_d^{(\alpha,\beta)}(R_{\alpha\beta}) = \frac{1}{4\pi^2}\int_{\mathbf{k}} d\mathbf{k}\Big\{\mathbf{q}_d^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta})\cdot\mathbf{q}_d^{(\alpha,\beta)}(-\mathbf{k},R_{\alpha\beta}) - \mathbf{q}_d^{(\alpha,\beta)}(\mathbf{k},\infty)\cdot\mathbf{q}_d^{(\alpha,\beta)}(-\mathbf{k},\infty)\Big\} \tag{6a}$$

for the interaction matrix $\mathbf{v}_d^{(\alpha,\beta)}(R_{\alpha\beta})$, where

$$\mathbf{q}_d^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta}) = \langle \Psi^{(\alpha,\beta)}(i,j)|\sum_p (q_p/k)e^{i\mathbf{k}\cdot\mathbf{r}_p}|\Psi^{(\alpha,\beta)}(i,j)\rangle \tag{6b}$$

is the previously defined spectral response matrix in the diatomic basis [2], and the sum over particles (p) in Eq. (6b) includes all electrons ($q_p = -e$) and nuclei ($q_p = +Z_\alpha e$ and $+Z_\beta e$) in the molecule. Equations (6a) and (6b) follow from the Fourier transform of the interaction operator appearing in Eq. (5b). In the limit of large internuclear separation ($R_{\alpha\beta}\to\infty$)

$$\mathbf{q}_d^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta}\to\infty) \to \mathbf{M}^\dagger\cdot\mathbf{q}_{sp}^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta})\cdot\mathbf{M}, \tag{7}$$

where $\mathbf{q}_{sp}^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta})$ is the spectral response matrix in the pair product basis, and $\mathbf{M}$ is a known constant matrix that accounts for possible diatomic state degeneracy in the large $R_{\alpha\beta}$ limit. Accordingly, the calculated diatomic eigenstates are seen to provide the spectral response matrix in both diatomic and spectral-product representations, which matrices can be employed to determine the unitary transformation matrix $\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta})$ that connects them

$$\mathbf{q}_{sp}^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta}) = \mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta})^\dagger\cdot\mathbf{q}_d^{(\alpha,\beta)}(\mathbf{k},R_{\alpha\beta})\cdot\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta}). \tag{8}$$

It is seen from the expression of Eq. (6a) that the transformation of Eq. (8) also provides the transformation of Eqs. (5). Because the transformation matrix $\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta})$ satisfying Eq. (5a) also satisfies Eq. (8), the latter provides necessary and sufficient conditions for determination of the transformation from the physically meaningful diatomic states to the spectral-product basis.

IV. Illustrative Applications - $NaAr_N$ Clusters

Applications of the foregoing development are reported for physically bonded Ar_N clusters seeded with Na atoms. For this system, the rotations [Eq. (8)] are solved in the $\mathbf{k} \rightarrow 0$ limit, appropriate for long-range interactions, in which case $\mathbf{q}_d^{(\alpha,\beta)}(\mathbf{k}, R_{\alpha\beta})$ becomes the diatomic dipole transition matrix $\boldsymbol{\mu}_d(R_{\alpha\beta})$, and $\mathbf{q}_{sp}^{(\alpha,\beta)}(\mathbf{k}, R_{\alpha\beta})$ becomes the corresponding dipole transition matrix, $\boldsymbol{\mu}_{sp}(R_{\alpha\beta})$, in the spectral-product basis. Solution of Eq. (8) is obtained in the form

$$\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{U}_d^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{U}_{sp}^{(\alpha,\beta)}(R_{\alpha\beta})^{\dagger}, \tag{9}$$

where $\mathbf{U}_d^{(\alpha,\beta)}(R_{\alpha\beta})$ is the unitary matrix that diagonalizes $\boldsymbol{\mu}_d(R_{\alpha\beta})$ and $\mathbf{U}_{sp}^{(\alpha,\beta)}(R_{\alpha\beta})$ is the unitary matrix that diagonalizes $\boldsymbol{\mu}_{sp}(R_{\alpha\beta})$. Equation (9) is valid in the limit that closure has been achieved in the diatomic and spectral-product representations and the eigenvalues of $\boldsymbol{\mu}_d(R_{\alpha\beta})$ and $\boldsymbol{\mu}_{sp}(R_{\alpha\beta})$ are accordingly identical.

Employing the transformation of Eq. (9) in Eq. (5a) gives the final expression

$$\mathbf{v}_{sp}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) = \mathbf{T}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta})^{\dagger} \cdot \mathbf{E}_d^{(\alpha,\beta)}(R_{\alpha\beta}) \cdot \mathbf{T}^{(\alpha,\beta)}(\boldsymbol{R}_{\alpha\beta}) - \mathbf{E}_d^{(\alpha,\beta)} \tag{10}$$

for the pair-interaction matrices, where the substitution $\hat{V}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}) = \hat{H}^{(\alpha,\beta)}(\boldsymbol{i};\boldsymbol{j}) - \hat{H}^{(\alpha)}(\boldsymbol{i}) - \hat{H}^{(\beta)}(\boldsymbol{j})$ has been employed, $\mathbf{E}_d^{(\alpha,\beta)}(R_{\alpha\beta})$ is the diagonal matrix of diatomic energies, and $\mathbf{E}_d^{(\alpha,\beta)}$ is its $R_{\alpha\beta} \rightarrow \infty$ limit.

In Fig. 1 are shown diatomic potential energy curves for the ground and low-lying excited states of $NaAr$ calculated as functions of internuclear distance employing multi-reference configuration-interaction methods [14]. Evidently, the excited F and H states undergo an avoided crossing, whereas the other states within a symmetry class (Σ, Π, Δ) are generally well separated at all $R_{\alpha\beta}$. The associated electric dipole and transition matrix elements required in Eq. (8), shown in Figs. 2 and 3 for selected Σ and Π states, are seen to be strong functions of internuclear separation, consequent of atomic-product-state mixings at all $R_{\alpha\beta}$. Also shown in these figures are the eigenvalues of the matrices $\boldsymbol{\mu}_d(R_{\alpha\beta})$ for Σ and Π states, which are significantly less dependent upon internuclear separation than are the matrix elements themselves. Moreover, these eigenvalues are in very good accord with those of the matrices $\boldsymbol{\mu}_{sp}(R_{\alpha\beta})$, which are also shown in the figures, and which should be entirely independent of $R_{\alpha\beta}$. In the limit of closure in the diatomic and spectral-product basis sets, the eigenvalues of the two matrix representatives of the transition moment operator become identical and independent of $R_{\alpha\beta}$.

The transformation matrices obtained for Na-Ar interactions from the results of Figs. 1 to 3 and Eqs. (6) to (10) with $\mathbf{k} \rightarrow 0$ are employed in calculations of potential energy surfaces for the aggregates of interest, whereas the Ar-Ar interactions are treated as pair-wise additive in the ground-state potentials. Note that the matrix $\mathbf{M}$ becomes the unit matrix for the states of interest in $NaAr$. In Fig. 4 are shown sections of the potential energy surfaces of $NaAr_2$ (C_{2v} symmetry) as functions of the Ar-Na-Ar angle for states associated with Na $3s \rightarrow 3d, 4p$ excitations. Also shown in the figure are the corresponding

states obtained from the present development employing a unit matrix for the required transformation $[\mathbf{U}^{(\alpha,\beta)}(R_{\alpha\beta}) = \mathbf{1}]$, which corresponds to the so-called Balling & Wright approximation commonly employed in collisional broadening studies and trapped radical spectroscopy [3]. Evidently, the spectral method provides avoided crossings in the calculated $^2A_1$ and $^2B_2$ energy surfaces associated with $Na\ 3s \rightarrow 3d, 4p$ excitations, whereas the simpler model does not. Similar observations apply to the more complicated energy surfaces for larger $NaAr_N$ aggregates, also obtained from the present development employing the single *Na-Ar* transformation matrix of Eqs. (9) and (10). These results suggest that non-additive contributions to the potential energy surfaces of large van der Waals aggregates can be determined quite generally in terms of the underlying pairwise-interaction matrices by employing the computational prescription of Eqs. (9) to (10) for constructing the required pair transformation matrices. In the case of chemical interactions, the more general spectral response matrices of Eqs. (6) to (8) are preferred over the dipole matrices employed for van der Waals aggregates.

V. Concluding Remarks - General Implementation and HEDM Applications

The spectral method and procedures described here for computational implementations have been employed in studies of the effects of non-additivity in the potential energy surfaces on the structure and optical absorption spectra of $NaAr_N$ [N= 2 to 147] van der Waals aggregates, results that will be reported subsequently. Some indication of the nature of the approach is provided by the illustrative results reported in Figs. 1 to 4, which employ a limit ($\mathbf{k} \rightarrow 0$) appropriate for long-range interactions. Evidently, avoided crossings are obtained from the spectral method in the potential surfaces of these aggregates employing accurate diatomic potential curves.

When the development of Eqs. (6) to (10) is employed, rather than the dipole limit employed in the applications reported here, the spectral method and its implementation is generally applicable to both physical and chemical interactions. Evaluation of the spectral response matrix of Eqs. (6a) and (6b) in the large electronic basis sets required for diatomic calculations will entail development of appropriate computer code routines for this purpose. Additionally, adoption of previously described Stieltjes methods for construction of complete sets of spectral states will allow applications of the spectral method in the limit of closure [15]. These issues are presently under study and will be topics of subsequent HEDM reports.

Applications of the spectral method are in progress to potential cryogenic HEDM systems which may improve the specific impulse of H_2/O_2 propulsion systems. Specifically, the potential energy surfaces of $Li(H_2)_N$ and $Al(H_2)_N$ aggregates are under study in order to clarify the natures of the physical (van der Waals) trapping sites in these cases, and to determine stabilities of the trapping configurations to chemical reactions that can produce the stable products *LiH* and *AlH* when the aggregates are subjected to thermal or other influences. Additionally, in view of the importance of cryogenic He_N clusters as potential vehicles for pickup and transport of trace metals into cryogenic fuel or oxidizer matrices, studies of the potential energy surfaces of $LiHe_N$ and $AlHe_N$ aggregates will be undertaken.

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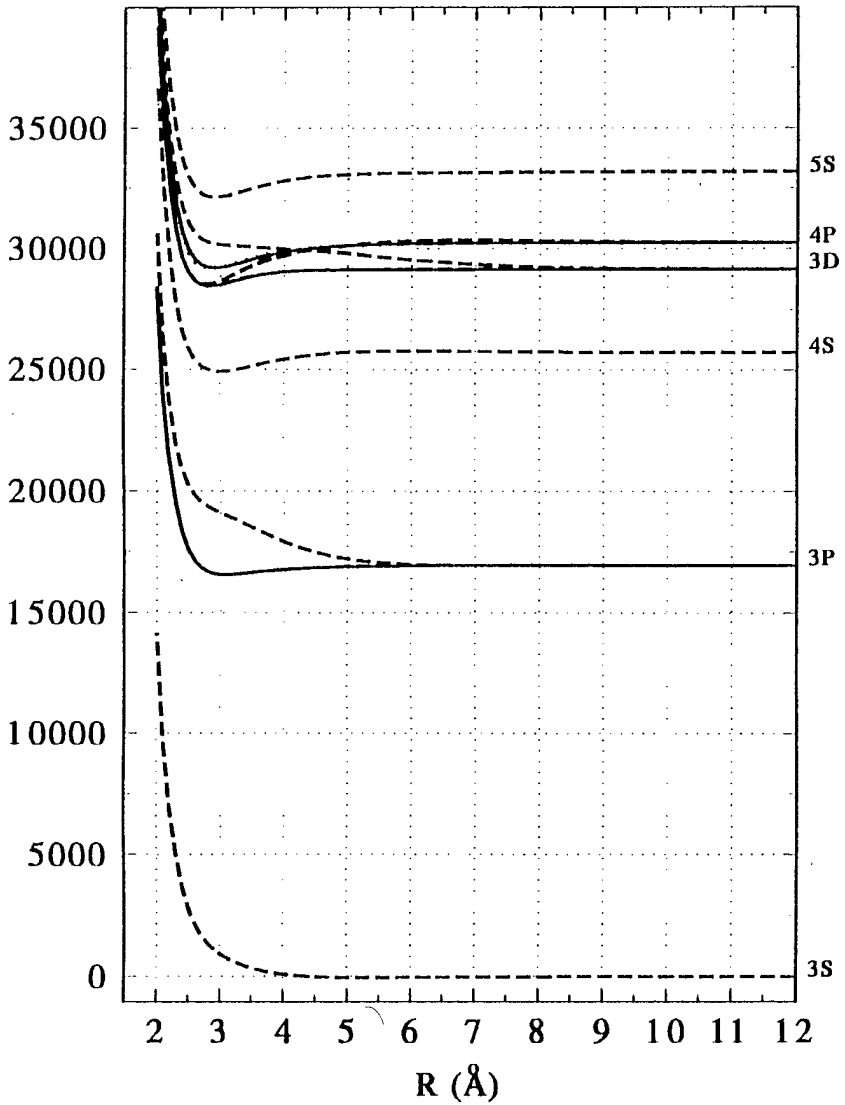

Figure 1. Potential energy curves for the ground- and low-lying-excited states of *NaAr* obtained from multi-reference configuration-interaction calculations [14]; (- - -) Σ states; (—) Π states; (· · ·) Δ state.

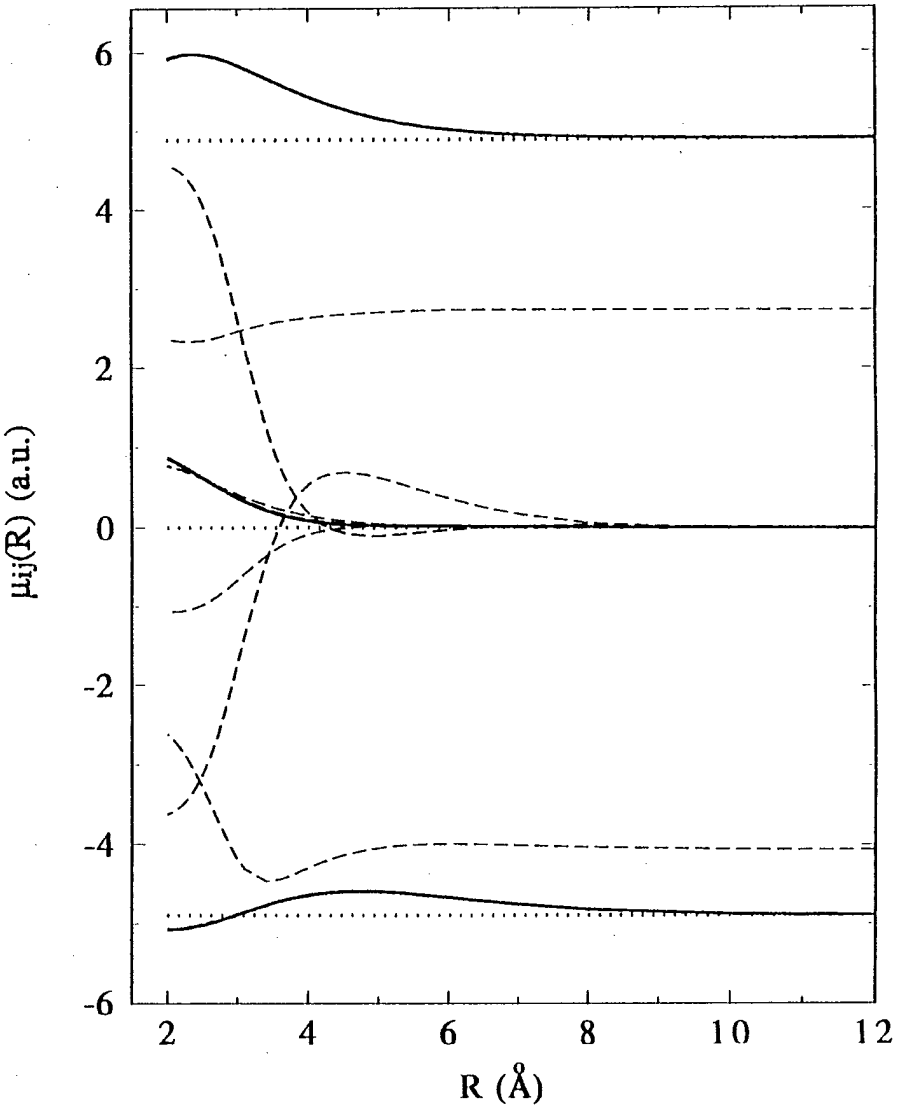

Figure 2. Electric-dipole and dipole transition matrix elements (- - -) for *NaAr* Π states obtained from the calculations reported in Fig. 1. Also shown are the eigenvalues of the transition matrices in the diatomic (—) and spectral product (· · ·) representations.

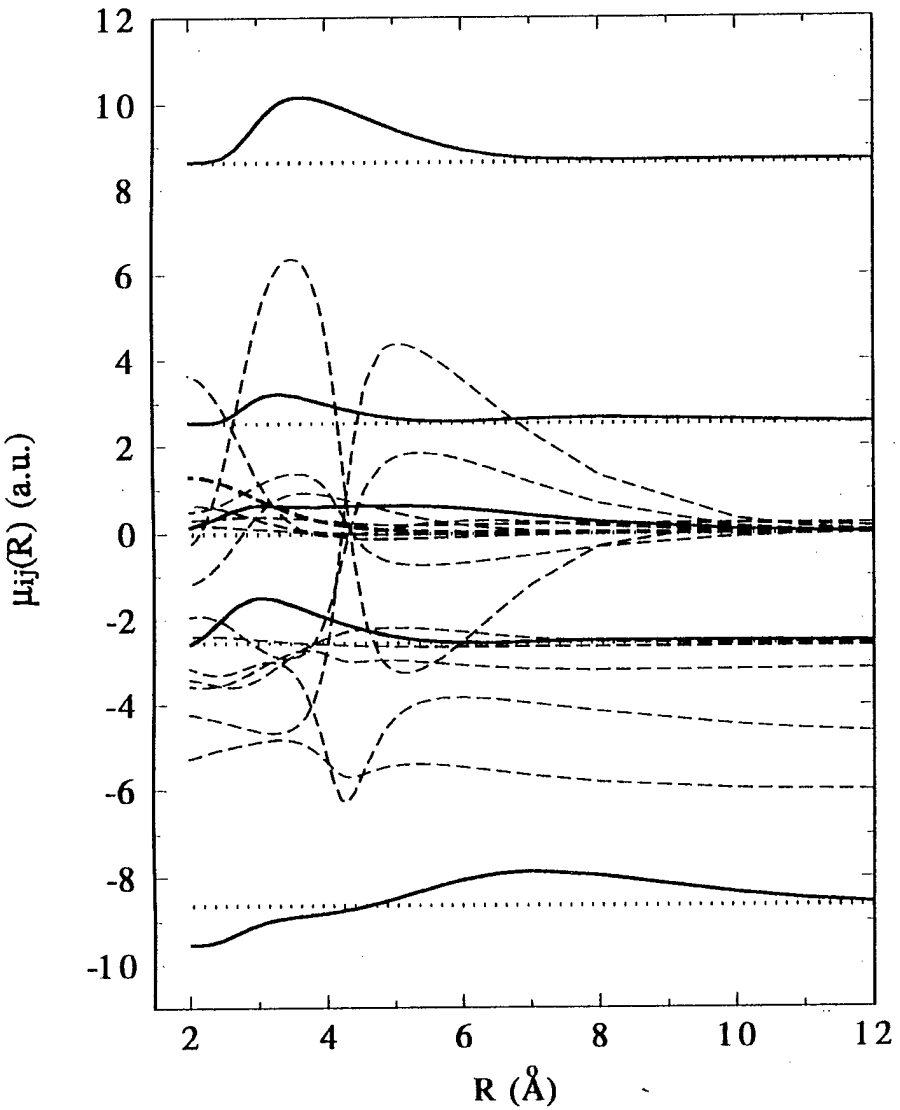

Figure 3. Electric-dipole and dipole transition matrix elements (- - -) for $NaAr$ Σ states obtained from the calculations reported in Fig. 1. Also shown are the eigenvalues of the dipole transition matrices in the diatomic (—) and spectral product ($\cdots$) representations.

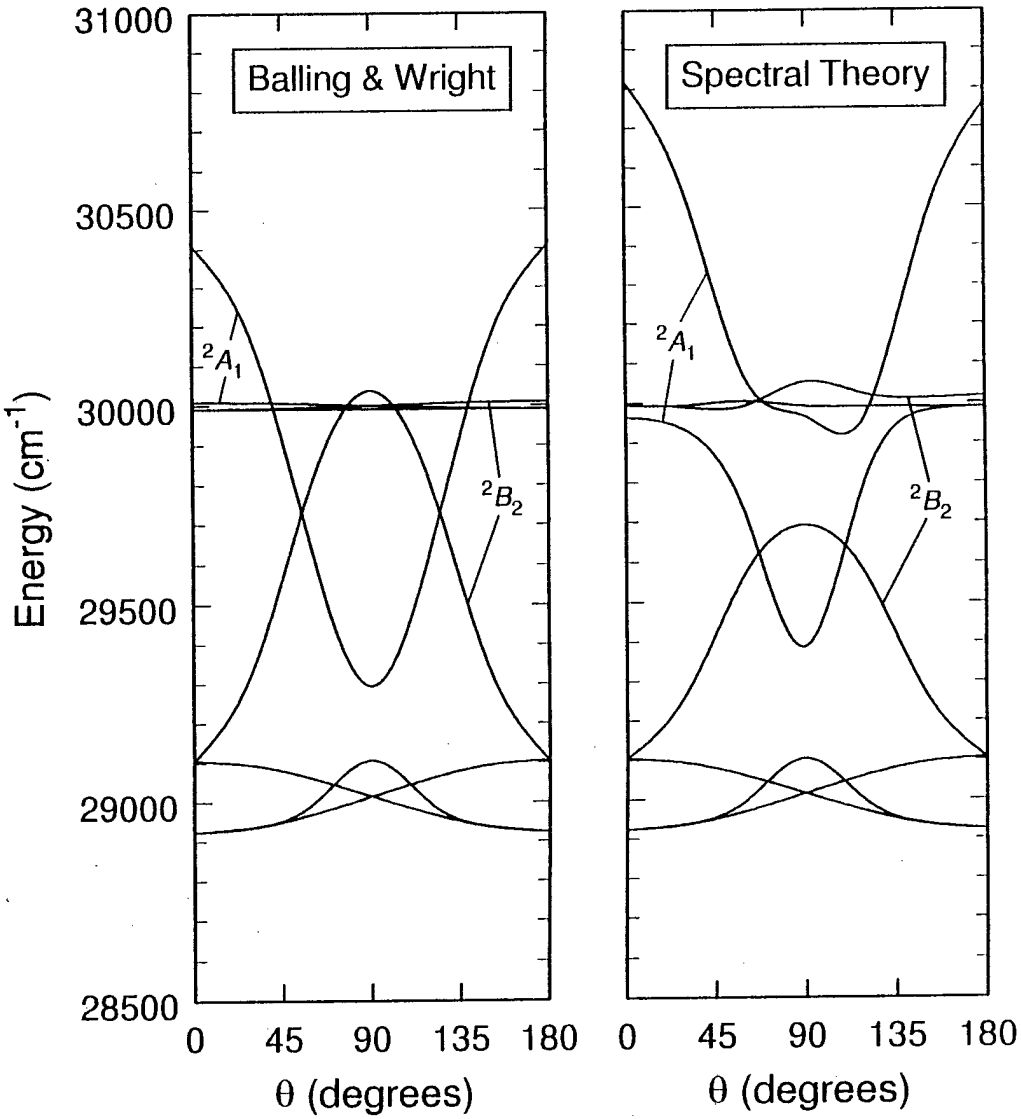

Figure 4. Potential energy surfaces for C_{2v} symmetry $NaAr_2$ as functions of the molecule apex angle: Balling & Wright - values obtained employing a unit matrix in place of the transformation of Eq. (9); Spectral Theory - values obtained from the spectral method employing the unitary transformation of Eq. (9).